U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB80-146319

Status Assessment of Toxic Chemicals Arsenic

Monsanto Research Corp, Dayton, OH

Prepared for

Industrial Environmental Research Lab -Cincinnati, OH

Dec 79

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-79-210b
December 1979

Research and Development

PB80-146319

EPA

Status Assessment of Toxic Chemicals

Arsenic

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TECHNICAL REPORT DATA

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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-79-210b		PB80-146319

4. TITLE AND SUBTITLE

Status Assessment of Toxic Chemicals: Arsenic

5. REPORT DATE

December 1979 issuing date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

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10. PROGRAM ELEMENT NO.

1AB604

11. CONTRACT/GRANT NO.

68-03-2550

12. SPONSORING AGENCY NAME AND ADDRESS

Industrial Environmental Research Lab. - Cinn, OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED

Task Final 11/77 - 12/77

14. SPONSORING AGENCY CODE

EPA/600/12

15. SUPPLEMENTARY NOTES

IERL-Ci project leader for this report is Dr. Charles Frank, 513-684-4481

16. ABSTRACT

The production, consumption, and uses of arsenic are dealt with in this report. Sources of environmental contamination by arsenic are identified and the consequences of such pollution explained. Better control methods are needed for both air emissions and discharge of arsenic-containing wastewaters. Present control technologies are listed as well as areas in which further study is required.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Arsenic, metalloids, Arsenic Isotopes, Arsenic Organic Acids, Arsenic Organic Compounds, Arsine, Arsenides, Arsenic Oxides, Arsenic Inorganic Compounds, Arsenic Halides, Arsenic Containing Alloys, Arsenic Chlorides, Arsenic Trioxide, Arsenic Metal	Pesticides, Smelting, Copper	68A 68D 68G

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

* U.S. GOVERNMENT PRINTING OFFICE 1980-657-146/5508

EPA-600/2-79-210b
December 1979

STATUS ASSESSMENT OF TOXIC CHEMICALS: ARSENIC

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of arsenic. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
Director
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ABSTRACT

Arsenic, which is found naturally in metal ore deposits, is produced commercially as a byproduct during the processing of nonferrous metal ores. Estimated 1974 consumption of arsenic in the United States was 22,300 metric tons with the sole U.S. producer, the ASARCO copper smelter in Tacoma, Washington, supplying approximately 8,700 metric tons (as arsenic trioxide).

In addition to arsenic trioxide and arsenic metal, there are at least 45 other arsenic compounds of commercial significance produced in the U.S. The largest use of arsenic is in the production of agricultural pesticides, which includes herbicides, insecticides, desiccants, wood preservatives, and feed additives.

It is recognized that atmospheric emissions of arsenic from smelting operations constitute a major pollutant source. Substantial amounts of arsenic escape to the atmosphere from pyrometallurgical copper operations. An estimated 4,500 metric tons of arsenic were released to the atmosphere in 1976 by primary nonferrous smelters; nearly 90% of this total was a result of copper production. Other emission sources include lead and zinc smelters, glass production plants, coal burning facilities, arsenical compound production plants, and pesticide application. Evidence indicates that disposal of high arsenic-containing wastewater and solid wastes has a potential impact greater than that of air emissions. One veterinary pharmaceuticals plant has been measured with a raw waste loading of 10,000 g/m^3 arsenic and 50 g/m^3 to 60 g/m^3 after treatment.

Since arsenic is a suspected carcinogen, regulations have been or are being established for human exposure in air and water. Two arsenical pesticides have recently had their registrations cancelled. Based upon the information presented in this report, several items should be considered in future studies. Control methods are needed for arsenic fume and fugitive emissions from pyrometallurgical smelter operations, and treatment methods are needed for discharge of high arsenic-containing wastewaters. Production statistics and process information is needed to better understand the production of arsenicals, and fixation and disposal of high arsenic-containing solid wastes should be studied including leaching from existing sites.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Pound-mass	2.205×10^{3}
Pascal (Pa)	Torr (mm hg, 0°C)	7.501×10^{-3}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\epsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

ACKNOWLEDGEMENT

This report was assembled for EPA by PEDCo-Environmental, Inc., Cincinnati, OH, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

SECTION I

INTRODUCTION

Arsenic, a suspected human carcinogen, is ubiquitous in the environment. It is produced commercially as a byproduct during the processing of nonferrous metal ores and naturally occurs in these metal ore deposits. There is a concern of adverse human health effects from inorganic arsenic due to its suspected carcinogenicity.

There is a need to define the various sources from which arsenic may be mobilized in the environment, to establish the consequent health and environmental effects, and to examine possible control techniques and present regulatory actions. This report provides a brief overview describing these items with emphasis on arsenic sources and the resulting environmental significance. Producers, production process, and uses of arsenic are also discussed.

SECTION 2

SUMMARY

Arsenic is produced commercially as a byproduct during the processing of nonferrous metal ores, with which it is associated in natural deposits. The ASARCO copper smelter in Tacoma, Washington is the sole domestic production site for arsenic metal and arsenic trioxide, from which all other arsenic compounds are produced. While production information at Tacoma is proprietary, it is estimated that in 1974 approximately 8,700 metric tons of arsenic (as arsenic trioxide) were produced. Estimated 1974 United States consumption was 22,300 metric tons, with the balance of demand over domestic production met by imports.

The domestic recovery process for arsenic consists of placing the concentrates and raw materials into a roaster, in which they are heated to between 650°C and 700°C until the arsenic vaporizes. Gases from the roaster are condensed in two series of brick cooling chambers, yielding a product containing 90% to 95% arsenic trioxide. Greater purity arsenic trioxide product is produced by resublimation in a reverberatory furnace at approxmately 538°C, followed by recondensation. Arsenic metal is occasionally produced at Tacoma by reducing the oxide with carbon in an oxygen deficient atmosphere. Table 1 is a summary of highlighted information regarding arsenic presented in this report.

In addition to arsenic trioxide and arsenic metal, there are at least 45 other arsenic compounds of commercial significance produced in the United States. The largest use of arsenic is in the production of agricultural pesticides, which include herbicides, insecticides, desiccants, wood preservatives, and feed additives.

Substantial amounts of arsenic are escaping into the atmosphere from pyrometallurgical copper operations. An estimated 4,500 metric tons of arsenic were released to the atmosphere in 1976 by primary nonferrous smelters; nearly 90% of this total resulted from copper production. While it is recognized that the atmospheric emissions of arsenic from smelting operations constitute a major pollution source, evidence indicates that the disposal of high arsenic-containing wastewater and solid waste has a potential impact greater than that of air emissions. An investigation of a plant producing veterinary pharmaceuticals and intermediate organic chemicals including arsenicals has been

TABLE 1. ARSENIC

Emission source	Emission quantity	Population exposed	Control method	Regulatory action
Production:				
Off-gas from primary copper, lead, and zinc smelting	4,500 metric tons/yr (90%, 5%, and 5% from copper, lead and zinc smelting, respectively).	Some smelters are near population centers.	Mechanical collectors, heat exchangers, electrostatic precipitators (all are relatively inefficient 8 - 26%).	Workplace exposure limit of 4 $\mu g/m^3$ at 8 hr (Occupational Safety and Health Administration). (This may be reduced).
Arsenic trioxide (8,700 metric tons, 1974)	Air and water emissions occur - quantities unknown.	Produced only at Tacoma, Washington.	Neutralization, precipitation, pond sealing, sludge disposal (landfill).	10 ppm in effluent under EPA effluent guidelines (Best Practicable Technology). Office of Air Quality Planning and Standards is considering an ambient air standard for arsenic in 1978.
Arsenic metal	Waste water from ASARCO. Tacoma has been measured at 310 g/m^3 arsenic.	Produced only at Tacoma, Washington.	No data available.	
Transportation:				
Cleaning of transport vehicles	Unknown.	Unknown.	Neutralization, precipitation, pond sealing, sludge disposal (landfill).	
Leachate landfill	The amount is expected to be quite large.	Problem centers lie in watersheds on or near landfill sites.	Unknown.	Possible regulation may occur under the Safe Drinking Water Act.
Industrial use: (Consumption, 1974 - 22,300 metric tons, for all uses)				
Arsenic metal: Metallurgical additives (3%)	A veterinary pharmaceuticals plant has been measured with a raw waste loading of 10,000 g/m^3 arsenic and 50 - 60 g/m^3 after treatment.	No data available.	Standard waste treatment methods are assumed, but may not be adequate.	Basic copper arsenate and copper acetoarsenite have been cancelled for pesticide usage under Federal Insecticide, Fungicide, and Rodenticide Act.
Arsenic compounds: Insecticides (22%) Herbicides (23%) Desiccants and defoliants (~15%) Soil sterilizers (17%) Glass additives (10%) Miscellaneous (10%)				Arsenic is also a priority pollutant for study under the Federal Water Pollutant Control Act.
Consumer use of end products:				
Application of arsenical pesticides	Unknown.	Unknown.		Possible regulation under Federal Insecticide, Fungicide, and Rodenticide Act.
Public exposure due to use of products	Unknown.	Unknown.		

conducted by the EPA. The plant produces two major wastewater streams, one which contains about 10,000 g/m^3 total arsenic and 6,000 g/m^3 organics at a flow rate of 75.7 m^3/day. The treated stream contains 50 g/m^3 arsenic and it is clarified, neutralized, settled, and then routed to the city sewer where sludges are landfilled. Also, there is increasing evidence to indicate that there may be serious environmental problems by the production of arsenical pesticides. Since arsenic is a suspected carcinogen, epidemiological analyses should be conducted to support previous findings of high incidences of lung cancer in smelter workers and high arsenic in the urine of both workers and children living near smelters.

The Environmental Protection Agency (EPA) is considering the development of regulations under the Clean Air Act. The Office of Air Quality Planning and Standards has tentative plans for promulgating an arsenic standard in 1978. Two registered arsenical pesticides have recently had their registrations cancelled. The Occupational Safety and Health Administration (OSHA) has set a workplace exposure limit of 4 $\mu g/m^3$, which may be downgraded in the near future. Arsenic is a consent decree compound and is thus destined for regulation under that agreement. Best Practicable Technology (BPT), as established by the Effluent Guidelines Division (EGD) of EPA, for the nonferrous metals industry lists an average effluent concentration of 10 ppm. Finally, regulation of arsenic under the Safe Drinking Water Act is anticipated.

Based upon the information presented in this report, the following items need to be considered in future studies:

- Methods for control of arsenic fume and fugitive emissions from pyrometallurgical smelter operations, including assessments of the adequacy of commercially-available control devices, new control technology options, and the ultimate fate of arsenic with the various control technology options.

- Treatment methods for high-arsenic wastewater discharged from both smelters and plants producing arsenic compounds.

- Fixation and disposal of high-arsenic solid wastes including leaching from existing disposal sites.

- Improved understanding of the production of arsenicals--production processes, waste streams, control technologies, and end uses. Visits to production facilities in the industry could provide much of this understanding. Highest priority would be assigned to those companies with a varied product slate of arsenicals. However, representative smaller producers should not be overlooked, as any production process involving arsenic compounds can result in fugitive emissions and wastes with serious environmental consequences.

- Environmental behavior of arsenic and arsenic compounds.
- Production statistics, locations and present waste treatment configurations for the many end use arsenicals.
- Epidemiological analyses investigating high incidences of lung cancer in smelter workers and high arsenic in the urine of both workers and children living near smelters.

SECTION 3

SOURCE DESCRIPTION

Arsenic is produced commercially as a byproduct during the processing of nonferrous metal ores, with which it is associated in natural deposits. Arsenic occurs primarily as inorganic compounds; it occurs very infrequently in the elemental state. It also forms a variety of organic compounds; i.e., compounds containing an arsenic-carbon bond. Both organic and inorganic arsenic compounds can be toxic to man, and inorganic arsenic compounds have been associated with lung cancer in worker populations (1).

PRODUCTION

Table 2 lists the 29 domestic primary nonferrous smelters, indicating the principal likely sources of atmospheric arsenic emissions for each. Arsenic sublimes at temperatures lower than the operating temperatures of most existing particulate control devices, so most arsenic in the concentrate is driven off during the first high-temperature contact. Figure 1 (2) locates these facilities.

The ASARCO copper smelter in Tacoma, Washington, is the sole domestic production site for arsenic metal and arsenic trioxide, from which all other arsenic compounds are produced. The feed to Tacoma includes concentrates containing a high proportion of arsenic (3% to 15%), as well as intermediate products such as flue dusts, speisses, and other high-arsenic residues (5% to 30% arsenic) from other nonferrous smelters. Since the supply of domestic arsenic exceeds its demand, only a portion of the high-arsenic residues are shipped to Tacoma; the rest are disposed of or stored at the smelters. Production information at Tacoma is proprietary, but the estimated 1974 production of arsenic (as

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(1) Arsenic Sources and Control Technology Review. Contract No. 68-01-2984, U.S. Environmental Protection Agency, Cincinnati, Ohio, July 1976.

(2) Davis, W. E., et al. National Inventory of Sources and Emissions-1968. Contract No. CPA 70-128 (PB 220 619), U.S. Environmental Protection Agency, Durham, North Carolina, May 1971. 60 pp.

TABLE 2. PRIMARY COPPER, LEAD, AND ZINC SMELTERS

Company	Location	Principal product metal	Capacity metric tons/yr	Likely sources of arsenic emissions			
				Roasting furnaces	Sinter machines	Blast furnaces	Smelting furnaces
Amax, Inc.	East St. Louis, IL	Zinc	76,000	x			
Amax - Homestake Lead Tollers	Boss, MO	Lead	127,000		x	x	
The Anaconda Co.	Anaconda, MT	Copper	180,000	x			x
Asarco, Inc.	Tacoma, WA	Copper	91,000	x			x
	El Paso, TX	Copper	104,000	x			x
		Lead	109,000		x	x	
	Hayden, AZ	Copper	163,000	x			x
	East Helena, MT	Lead	109,000		x	x	
	Glover, MO	Lead	100,000		x	x	
	Corpus Christi, TX	Zinc	98,000	x			
	Columbus, OH	Zinc oxide	20,000	x	x		
The Bunker Hill Co.	Kellogg, ID	Lead	118,000		x	x	
		Zinc	98,000	x			
Cities Services Co.	Copperhill, TN	Copper	20,000	x			x
Copper Range Co.	White Pine, MI	Copper	82,000				x
Inspiration Consolidated Copper Co.	Miami, AZ	Copper	64,000				x
Kennecott Copper Corp.	Garfield, UT	Copper	254,000				x[a]
	Hurley, NM	Copper	73,000				x
	Hayden, AZ	Copper	73,000	x			x
	McGill, NV	Copper	45,000				x
Magma Copper Co.	San Manuel, AZ	Copper	181,000				x
National Zinc Co.	Bartlesville, OK	Zinc	45,000	x			
New Jersey Zinc Co.	Palmerton, PA	Zinc	103,000	x	x		
Phelps Dodge Corp.	Morenci, AZ	Copper	161,000	x			x
	Douglas, AZ	Copper	115,000	x			x
	Hidalgo, NM	Copper	91,000				x
	Ajo, AZ	Copper	64,000				x
St. Joe Minerals Corp.	Herculaneum, MO	Lead	204,000		x	x	
	Monaca, PA	Zinc	227,000	x	x		

[a]The Kennecott-Garfield smelter is converted to the Noranda process, in which a single furnace combines most of the functions of roasting, smelting, and converting.

Figure 1. Primary United States nonferrous smelting locations (2).

arsenic trioxide) was 8,700 metric tons.[a] Estimated 1974 United States consumption was 22,300 metric tons, with the balance of demand over domestic production met by imports due to economic and purity considerations. Demand is expected to increase at 0.3%/yr through 1980. Sweden and Mexico, which together account for over half of world arsenic trioxide production, are the principal source of imports. Arsenic trioxide enters the United States duty-free. There are also minor imports of arsenic metal, on which there is a 2.6¢/kg duty. The United States holds about one-fourth of estimated world arsenic reserves.

PROCESS DESCRIPTION

Since most of the arsenic produced is in the form of arsenic trioxide (As_2O_3) as a byproduct of the smelting of other metals, the production of arsenic is closely associated with the recovery and treatment of arsenic-bearing flue dusts. As arsenic trioxide is volatilized during the smelting of copper, lead, zinc, and other metals, it is concentrated in this dust. The crude flue dust

[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages of this report.

carrying up to 30% arsenic trioxide may also contain oxides of copper or lead, and other metals such as antimony, zinc, and cadmium (2).

The crude flue dust recovered during the smelting operation is further refined by mixing it with a small quantity of pyrite or galena concentrate prior to roasting. The pyrite or galena prevents the formation of arsenites during roasting, and produces a clinkered residue suitable for return to the process for recovery of other metals. The gases from roasting are passed through a series of brick chambers or kitchens, in which the temperature varies from 221°C in the first, to 99°C or less in the last. As the gases cool, arsenic trioxide condenses as a crude white powder, 90% to 95% pure. Much of the product is used in this form without further refinement (2).

If higher purity is required, the refining is usually carried out in a reverberatory furnace at a roasting temperature of about 538°C. The vapors first pass through a settling chamber and then through a series of kitchens. In the settling chamber, the temperature is maintained above the condensation temperature of the trioxide. In the kitchens near the furnace a black, amorphous mass is condensed which contains about 95% arsenic trioxide. This product is reprocessed. The bulk of the trioxide is condensed in the other kitchens at temperatures ranging from 121°C to 182°C, and most of the dust which exits from the kitchens is caught in a baghouse. Some of the arsenic escapes, all that is in the vapor phase, plus a relatively small amount of the dust. Figure 2 shows the basic steps for production of arsenic trioxide.

In addition to arsenic metal and arsenic trioxide, there are at least 45 other arsenic compounds of commercial significance produced in the United States, all of which are made from arsenic trioxide. Table 3 presents a listing of 45 known commercial arsenic products, their end uses, producing companies, and production sites. These products are manufactured by 28 companies with production either in excess of 0.45 metric tons/yr or an annual value of at least $1,000. Seven of these facilities are in New Jersey, four in California, and three each in New York, Illinois, Texas, and Oklahoma. Information on production technologies and site-specific production stastistics is considered proprietary by the manufacturers; however, this information can be made available for regulatory purposes. Table 3 is not an exhaustive listing of all arsenicals; there may be other arsenic products that are made only occasionally in small batches and are, therefore, not generally considered commercial arsenic compounds. Table 4 lists 31 arsenic compounds that have been manufactured in the past but that are not believed to be in current commercial production; however, if any of these are produced occasionally in small lots, it is likely to be by companies listed in Table 3.

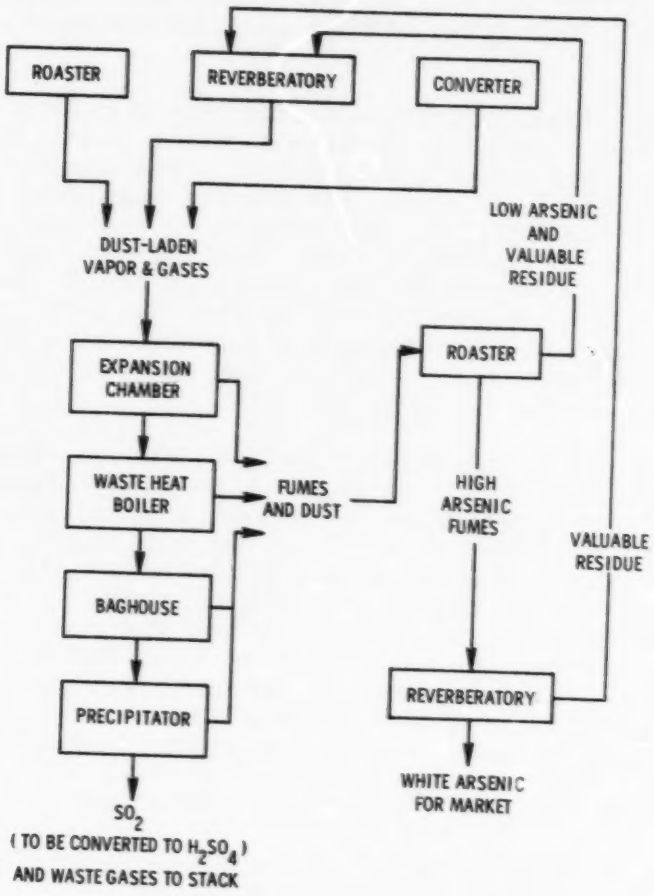

Figure 2. Flowsheet showing basic steps for production of arsenic trioxide at a copper smelter (2).

USES

The largest use of arsenic is in the production of agricultural pesticides, which includes herbicides, insecticides, desiccants, wood preservatives, and feed additives. Arsenic trioxide was the raw material for the older inorganic pesticides, including lead arsenate, calcium arsenate, and sodium arsenite. The newer major organic arsenical pesticides include three herbicides, monosodium and disodium methanearsonate (MSMA and DSMA) and cacodylic acid, and four feed additives that are substituted phenylarsonic acids. The organoarsenical segment of the pesticides industry produced approximately 15 products totaling 1.9×10^4 metric tons in 1973. This was an increase of almost 4.5×10^3 metric tons over 1972 production. Arsenic metal has several minor uses, primarily as an additive in metallurgic applications,

TABLE 3. ARSENIC COMPOUNDS

Chemical	Company	Location	Uses
Amine methanearsonate (AMA)	W. A. Cleary Corp. Vineland Chemical Co., Inc.	Somerset, NJ Vineland, NJ	Herbicide.
Antimony arsenate	City Chemical Corp.	Jersey City, NJ	
Arsambide (N-carbamoylarsonilic acid)	Eli Lilly & Co./Tippecanoe Labs Polychemical Labs, Inc. Rohm & Haas Co./Whitmayer Labs R.S.A. Corp.	Lafayette, IN Bronx, NY Myerstown, PA Ardsley, NY	Medicinal.
Arsanilic acid	Abbott Labs/Agri. & Vet. Prods. Fleming Labs, Inc.	North Chicago, IL Charlotte, NC	Arsanilates; mfg. of arsenical medicinal chemicals, veterinary medicine.
Arsaphen (acetarsone)	Sterling Drug, Inc./Winthrop Labs	Rensselaer, NY	Medicinal.
Arsenic	ASARCO, Inc.	Tacoma, WA	Metallic form: alloying additive for metals, especially lead and copper (shot, battery grids, cable sheaths, boiler tubes). High-purity (semiconductor) grade: used to make gallium arsenide for dipoles and other electronic devices; doping agent. in germanium and silicon solid state products; special solders medicine.
Arsenic acid	Los Angeles Chem. Co. Osmose Wood Preserving Co. Pennwalt Corp./Inorganic Chemical Woolfolk Chem. Works, Inc.	South Gate, CA Memphis, TN Bryan, TX Fort Valley, GA	Mfg. of arsenates; glass making wood treating process; defoliant desiccant for cotton; soil sterilant.
Arsenic iodide	City Chem. Corp.	Jersey City, NJ	Analytical chemistry, medicine.
Arsenic pentafluoride	Pennwalt Corp./Ozark-Mahoning Co.	Tulsa, OK	
Arsenic trifluoride	Pennwalt Corp./Ozark-Mahoning Co.	Tulsa, OK	

(continued)

TABLE 3 (continued)

Chemical	Company	Location	Uses
Arsenic trioxide	ASARCO, Inc.	Tacoma, WA	Pigments, ceramic enamels, aniline colors; decolorizing agent in glass; insecticide; rodenticide; herbicide; sheep and cattle dip; hide preservative; wood preservative; preparation of other arsenic compounds.
	Mallinckrodt Inc./Industrial Chem.	St. Louis, MO	
Arsine	Airco, Inc./Airco Industrial Gases G. D. Searle & Co./Matheson Gas	Santa Clara, CA Cucamonga, CA E. Rutherford, NJ Gloucester, MA Joliet, IL La Porte, TX Morrow, GA Newark, CA	Organic synthesis; military poison gas; electronics.
1,2-*Bis*(diphenylarsino) ethane	Pressure Chemical Co.	Ardsley, NY	
Bis(2-diphenylarsinoethyl) phenyl phosphine	Pressure Chemical Co.	Ardsley, NY	
1,2-*Bis*(diphenylarsino) methane	Pressure Chemical Co.	Ardsley, NY	
Cacodylic acid (dimethylarsinic acid)	The Ansul Co./Chem. Group Vineland Chem. Co., Inc.	Marietta, WI Vineland, NJ	Herbicide.
Cacodylic acid, sodium salt	Vineland Chem. Co., Inc.	Vineland, NJ	Herbicide, medicine.
Calcium arsenate	Los Angeles Chemical Co. Woolfolk Chem. Works, Inc.	South Gate, CA Fort Valley GA	Insecticide, germicide.
Calcium arsenite	Los Angeles Chemical Co.	South Gate, CA	Insecticide, germicide.
CAMA (calcium acid methyl arsenate)	Vineland Chem. Co., Inc.	Vineland, NJ	Herbicide.
Cobalt arsenate	City Chemical Corp.	Jersey City, NJ	Painting on glass; coloring glass.

(continued)

TABLE 3 (continued)

Chemical	Company	Location	Uses
Copper acetoarsenite	Los Angeles Chemical Co.	South Gate, CA	Wood preservative; larvicide.
Copper arsenate	City Chemical Corp.	Jersey City, NJ	Insecticide; fungicide.
Diphenylarsine	Pressure Chemical Co.	Ardsley, NY	
1-Diphenylphosphine-2-diphenylarsino ethane	Pressure Chemical Co.	Ardsley, NY	
DSMA (disodium methyl arsenate)	The Ansul Co./Chem. Group	Marietta, WI	Herbicide, pharmaceutical.
	W. A. Cleary Corp.	Somerset, NJ	
	Diamond Shamrock/Biosciences and Metals	Greens Bayon, TX	
	Vineland Chem. Co., Inc.	Vineland, NJ	
Gallium arsenide	Apache Chems., Inc.	Rockford, IL	Semiconductor in light-emitting diodes injection lasers; solar cells; magento-resistent devices; thermistors; microwave generation.
	Eagle-Picher Ind./Electronic Div.	Miami, OK	
		Quapaw, OK	
	Monsanto Co./Electronics Div.	St. Peters, MO	
Gallium arsenide phosphide	Monsanto Co./Electronics Div.	St. Peters, MO	Semiconductors.
Hexafluoro arsenic acid	Pennwalt Corp./Ozark-Mahoning	Tulsa, OK	
Indium arsenide	Monsanto Co./Electronics Div.	St. Peters, MO	Semiconductors; injection laser.
Lead arsenate	Dimensional Pigments, Inc.	Bayonne, NJ	Insecticide, herbicide.
	Los Angeles Chemical Co.	South Gate, CA	
	Rona Pearl, Inc.	Bayonne, NJ	
	Woolfolk Chemical Works, Inc.		
Lithium arsenate, primary	City Chemicals Corp.	Jersey City, NJ	
Methylarsine oxide	Vineland Chem. Co., Inc.	Vineland, NJ	Fungicide.
Methylarsine sulfide	Vineland Chem. Co., Inc.	Vineland, NJ	Fungicide.
MSMA (monosodium methyl arsenate)	The Ansul Corp./Chem. Group	Marietta, WI	Herbicide.
	Diamond Shamrock/Biosciences and Metals	Greens Bayon, TX	
	Vineland Chem. Co., Inc.	Vineland, NJ	

(continued)

TABLE 3 (continued)

Chemical	Company	Location	Uses
3-Nitro-4-hydroxyphenylarsonic acid	Salsbury Laboratories	Charles City, IA	Pharmaceutical.
4-Nitrophenylarsonic acid	Salsbury Laboratories	Charles City, IA	Pharmaceutical.
Potassium arsenate	City Chemical Corp.	Jersey City, NJ	Flypaper; insecticide; laboratory reagent preserving hides; printing textiles.
Potassium hexafluoroarsenate	Pennwalt Corp./Ozark-Mahoning	Tulsa, OK	
Silver arsenate	City Chemical Corp.	Jersey City, NJ	
Silver arsenite	City Chemical Corp.	Jersey City, NJ	Medicine.
Sodium arsanilate	Abbott Labs/Agri. & Vet. Prod.	North Chicago, IL	Medicine; veterinary medicine; organic synthesis.
Sodium arsenite	Rohm & Haas/Whitmoyer Labs	Myerstown, PA	Manufacturing
	Blue Spruce Co.	Bound Brook, NJ	Manufacturer of arsenical soaps for taxidermists; antiseptic; dying insecticides; hide preservation herbicide
	Los Angeles Chemical Co.	South Gate, CA	
	Pennwalt Corp./Inorganic Chem. Co.	Tacoma, WA	
	Woolfolk Chemical Works, Inc.	Fort Valley, GA	
Strychnine arsenate	City Chemical Corp.	Jersey City, NJ	
Triphenylarsine	Pressure Chemical Co.	Ardsley, NY	
Zinc arsenate	City Chemical Corp.	Jersey City, NJ	Insecticide; wood preservation.

TABLE 4. ARSENIC COMPOUNDS NOT CURRENTLY PRODUCED IN SIGNIFICANT QUANTITIES IN THE UNITED STATES

Compound	Use
Arsacetin	Medicine.
Arsenic disulfide	Depilatory agent; paints; rodenticides; glass.
Arsenic pentasulfide	Pigments; blue fire.
Arsenic pentoxide	Insecticide; dyeing and printing.
Arsenic thioarsenate	Thermal protectant.
Arsenic tribromide	Analytical chemistry, medicine.
Arsenic trichloride	Intermediate for organic arsenicals.
Arsenic trisulfide	Pigment; glass.
Arsphenamine	Medicine.
Arethinol	Medicine.
Ferric arsenate	Insecticide.
Ferric arsenite	Medicine.
Ferrous arsenate	Medicine, insecticide.
Magnesium arsenate	Insecticide.
Mercuric arsnilate	Medicine.
Mercuric arsenate	Medicine; paints.
Potassium arsenite	Medicine; mirrors.
Silver arsphenamine	Medicine.
Silver methylarsenate	Algicides.
Sodium arsenate	Medicine; insecticides; germicide, textiles.
Sodium arsphenamine	Medicine.
Strontium arsenite	Medicine.
Tryparsamide	Medicine.
Tetraarsenic tetrasulfide	Unknown.
Arsenic pentasulfide	Unknown.
Methanarsenic acid	Unknown.
Methyldihydroxyarsine	Unknown.
Dimethylhydroxyarsine	Unknown.
Trimethylarsine	Unknown.
Trimethylarsineoxide	Unknown.
Arsonic acids	Unknown.

in glass production, as a catalyst in several manufacturing processes, and in medicine. Arsenical drugs are still used in treating tropical diseases, such as African sleeping sickness and amebic dysentery, and are used in veterinary medicine to treat parasitic diseases, such as heartworm (filariasis) in dogs and blackhead in turkeys and chickens.

To summarize the end use information presented in Table 3, the 1974 demand for arsenic broke down as follows:

	Percent
Arsenic metal:	
Metallurgical additives	3
Arsenic compounds:	
Insecticides	22
Herbicides	23
Desiccant and defoliants	15
Soil sterilizers	17
Wood preservatives	6
Animal food additives	2
Glass additives	10
Miscellaneous	2

Although no single use dominates the market, the general category of pesticides includes 83% of the total. The production of arsenic metal has increased since 1974 when research indicated that it can impart strength to cast ferrous alloys. Chlorinated hydrocarbons are potential substitutes for arsenates in some applications, but restrictions on their use may inhibit extensive substitution.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Arsenic is not an abundant element, but it can be found in trace quantities almost everywhere since it is widely distributed in the earth's crust. It is present in sea water, in coal deposits, and in virgin soils as well as in ores. The most extensive occurrence is with copper, lead, cobalt, nickel, iron, gold, and silver (2).

Arsenic is generally regarded as a contaminant in ore and must be removed during smelting and refining in order to improve the quality of the metal; thus, arsenic emissions can occur during metallurgical processing. Figure 3 shows the sources of arsenic emissions incidental to processing nonferrous ores, from production of arsenic and arsenic compounds, and from the use of arsenical compounds. Figure 3 also indicates the media to which the arsenic is emitted.

Inorganic arsenic is emitted to the air from several sources, including copper, lead, and zinc smelters, glass production plants, coal-burning facilities, cotton gins, arsenical-compound (including pesticides) production plants, and pesticide application. Organic arsenic discharges are associated with the manufacture and use of pesticides. Trivalent arsenic which is a common contaminant of ores, occurs naturally and is the major component of arsenic emissions from smelters (3).

An environmental assessment of the primary copper, lead, and zinc industries concluded that substantial amounts of arsenic are escaping into the atmosphere from pyrometallurgical copper operations (4). Emissions are less significant in other copper processing steps or during lead and zinc smelting. An estimated 4,500 metric tons of arsenic were released to the atmosphere in 1976 by primary nonferrous smelters; nearly 90% of this total

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(3) Summary Characteristics of Selected Chemicals of Near-Term Interest. EPA-560/4-76-004 (PB 225 817), U.S. Environmental Protection Agency, Washington, D.C., April 1976. 50 pp.

(4) Environmental Assessment of Primary Copper, Lead and Zinc Industries, PedCo draft reports on Contract No. 68-02-1321 and 68-02-2535, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1978.

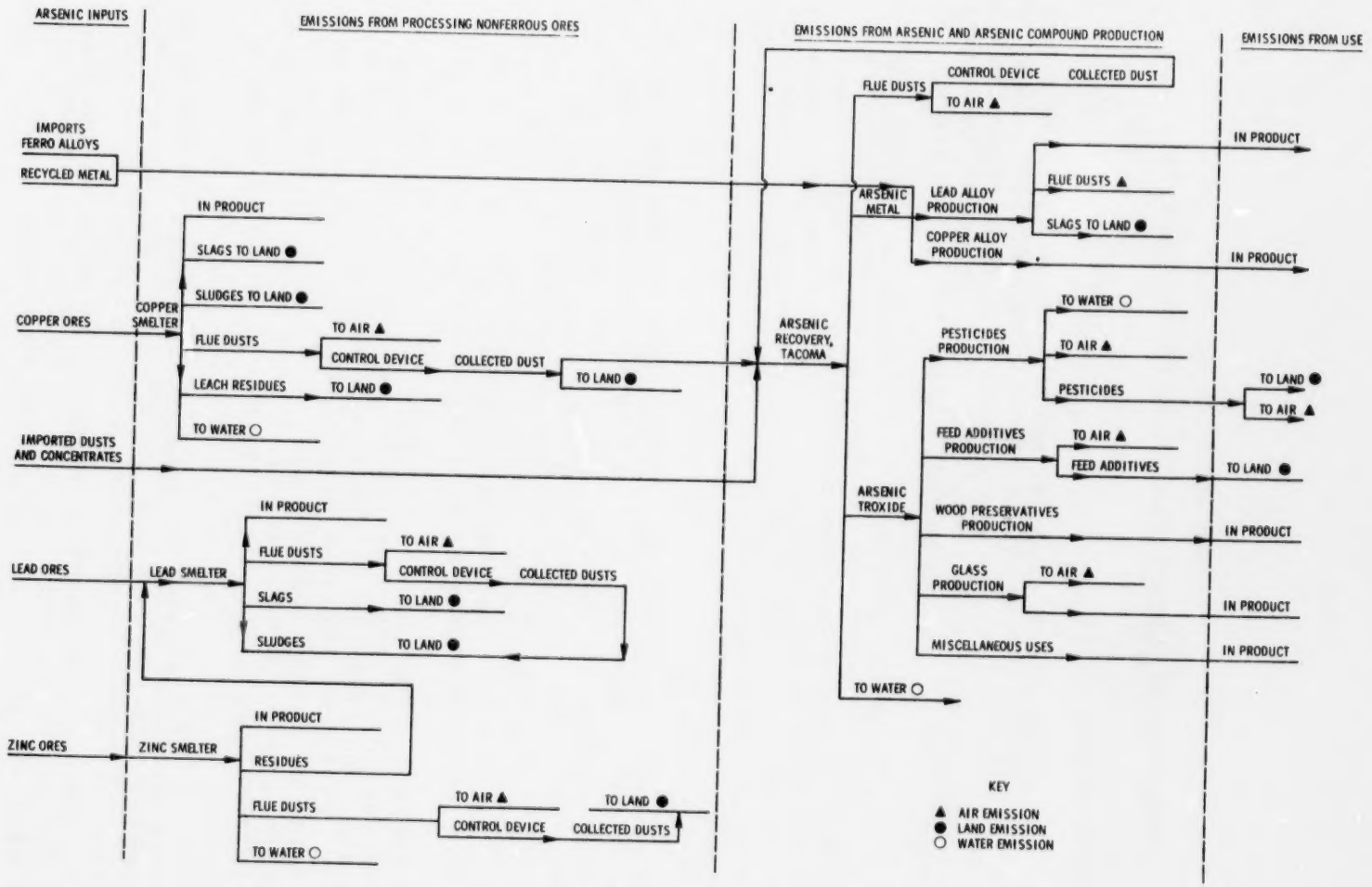

Figure 3. Flowsheet of arsenic emissions from production to use.

was a result of copper production. Land-destined wastes containing arsenic include flue dusts and residues from smelters, slags from steelmaking, and fly ash from coal combustion, as well as other minor sources. There is serious potential for environmental degradation by the leaching of these wastes into water supplies. Direct sources of arsenic into water include sulfuric acid plant blowdown and wastewater from various hydrometallurgical smelter processes. It is difficult to treat arsenic wastewater streams because of its solubility. The waste streams from arsenic recovery at ASARCO-Tacoma include the process gas stream (CO_2, H_2O, SO_2, arsenic fume), washdown water (310 g/m^3 arsenic), and fugitive dusts from materials handling. In many cases at nonferrous smelters, solid residues such as slags and dusts from gas cleaning operations are recycled. However, this practice can lead to the build-up of arsenic and other trace metals to unacceptable levels in the system, requiring the use of purge streams. These materials present a difficult disposal problem to prevent fugitive emissions or leaching into underground or surface waters.

An environmental assessment of the primary copper, lead, and zinc industries analyzes these industries as a series of interrelated production processes--45 for copper, 22 for lead, and 17 for zinc (4). Certain of these process steps for each industry involve the release of arsenic to various media. Each process is examined in terms of its function, input materials, operating conditions, utility consumption, waste streams, and control technology. The appendix is an example of a process description indicating the types of information presented.

While it is recognized that the atmospheric emissions of arsenic from smelting operations constitute a major pollutant source, evidence indicates that the disposal of high arsenic wastewater and solid waste has a potential impact of greater than that of the air emissions. Tables 5, 6, and 7 detail the magnitude and sources of arsenic discharged during nonferrous ore smelting (1). Proprietary limitations make it difficult to obtain detailed information regarding production processes and waste treatment configurations, not only in the nonferrous industry, but in end use of arsenicals as well. Characterization of waste streams in the end use industry is generally lacking, as most arsenicals are produced in batch lots at plants with many other products, and the effluents are often mixed prior to treatment and disposal.

There is increasing evidence to indicate that there may be serious environmental problems created by the production of arsenical pesticides. In one case, a pesticide manufacturer in Virginia sprayed high-arsenic wastes onto its property, which was in close proximity to the Potomac River. An analysis of the soil during a subsequent sale of the property revealed massive levels of arsenic contamination. At the request of the city, the soil was excavated, stored in sealed drums, and landfilled. The effects from the leaching of this material into the river are not known.

TABLE 5. DISTRIBUTION OF ARSENIC AT COPPER SMELTERS (1)

Arsenic containing source	Metric tons/yr
Lake copper product	30
Fire-refined copper product	6
Electrolytic copper product	7
Slags to land disposal	1,900
Sludges to land disposal	1,500
Flue dusts to land disposal	9,600
Lead residues dissipated to land	8,800
Treated wastewaters	32
Air emissions	4,800
Commercial white arsenic	8,300
TOTAL	35,000

TABLE 6. DISTRIBUTION OF ARSENIC AT PRIMARY LEAD SMELTERS (1)

Arsenic containing source	Metric tons/yr
Air emissions	240
Retained in refined lead	20
Land-destined solid wastes	800
TOTAL	1,060

TABLE 7. DISTRIBUTION OF ARSENIC AT ZINC CONCENTRATORS (1)

Arsenic containing source	Metric tons/yr
Air emissions	190
Retained in zinc products	5
Land-destined solid wastes	240
Wastewater effluents	0.4
Residues shipped to lead smelters	210
TOTAL	525

An investigation of a plant that produces veterinary pharmaceuticals and intermediate organic chemicals including arsenicals has been conducted by the U.S. EPA. The plant produces two major wastewater streams, one of which contains about 10,000 g/m^3 total arsenic and 6,000 g/m^3 organics at a flow rate of 75.7 m^3/day. This stream is treated by 2-stage batch precipitation using high-lime and manganous sulfate as precipitants. The treated wastewater, which contains 50 g/m^3 to 60 g/m^3 arsenic,

is clarified, neutralized, settled, and then routed to the city sewer where the sludges are landfilled. High concentrations of arsenic have been found in the municipal wastewater. A more extensive sampling and analysis program is scheduled, preliminary to the design of acceptable treatment methods.

The two preceding examples of arsenical production plants give some indication of the nature of the environmental problems that can arise at such facilities. Although little information is available, it is possible that many of the other production sites listed in Table 3 are creating similar problems.

Several arsenic cycles have been proposed to interrelate the sources, emissions, movement, distribution, and sinks of various forms of arsenic in the environment. Arsenic is continuously cycling in the environment, due to oxidation, reduction, and methylation reactions. The methylation process is a true detoxification, as methanearsonates and cacodylates are only one two-hundreth as toxic as sodium arsenite.

HEALTH EFFECTS

A health effects study of the primary copper, lead, and zinc industries was initiated recently by IERL-Ci. A comprehensive health effects literature search was followed by a retrospective epidemiological analysis comparing disease-specific mortality parameters for counties that have contained smelters for over 35 years to those for all surrounding counties. The results of this study indicate an observed incidence of various types of cancer in the counties with smelters that was higher than in the surrounding counties or the national average. Smelting zinc ore concentrates with high levels of arsenic was clearly associated with significantly elevated rates of cancer of the trachea, lung, and bronchus. The fact that arsenic is a suspected carcinogen would indicate that more definite studies of this nature should be undertaken. These data also support similar conclusions from a previous study that showed a high incidence of lung cancer in smelter workers and high arsenic in the urine of both the workers and children living near the smelter.

SECTION 5

CONTROL TECHNOLOGY

The method of treatment of the off-gases from high-temperature operations at nonferrous smelters varies, but the general patterns are the same. The gas is first passed through mechanical collectors and heat exchangers to remove large particles and reduce its temperature. Expansion chambers, balloon flues, cyclones, and waste heat boilers are all in use at primary copper smelters. Dust is finally collected in electrostatic precipitators; however, these devices are only partially effective for arsenic removal because their operating temperatures are above those necessary to effectively condense the arsenic fumes. Tests of a hot electrostatic precipitator on the reverberatory furnace at an Arizona copper smelter have indicated that only from 8% to 26% of the arsenic present in the concentrate fed to the furnace is being captured in this particular type of control device.

At the ASARCO-Tacoma smelter, the process gas from the arsenic plant is cleaned with an electrostatic precipitator, currently being replaced by a fabric filter. Fugitive emissions are controlled by fabric filters on the ventilation air. The controls in use at plants producing arsenic compounds are not known.

Fabric filters have higher efficiency that electrostatic precipitators, but they require 2 to 3 times the power and are also more expensive to purchase and install. They can be expected, however, to receive wider use as more complete arsenic control is required. High-pressure-drop venturi scrubbers are capable of effective removal of arsenic from a gas stream. They are now used at smelters to remove arsenic and other impurities in the gas which is fed to sulfuric acid manufacture equipment to prevent damage to the acid-producing catalyst. However, their use creates a water disposal problem. A copper smelter in Sweden achieves 98% arsenic removal from the combined gas stream from a roaster and electric smelting furnace in a 2-stage electrostatic precipitator with an intermediate cooling tower. Temperature control is critical, and the second stage operates at 130°C to 140°C to precipitate the majority of the sublimed arsenic. A 2-stage system using an electrostatic precipitator and fabric filter with intermediate cooling is also reported to be operating successfully at a Canadian smelter.

When considering the control of high-arsenic waste streams, it must be kept in mind that effective collection may create a waste disposal problem in another media. For example, because there is already an oversupply of arsenic, a disposal problem is created by collection of high-arsenic dusts in particulate control devices. Due to their slight solubility, these dusts can leach into streams and ground water supplies unless stored in weatherproof, siftproof silos, or in hopper cars. A major research program at Montana College of Mineral Science and Technology being conducted for IERL-Ci is investigating the fixation of arsenic wastes to permit their safe disposal.

As has been previously indicated, little is known about the control technologies in use at the plants producing the various arsenic compounds from arsenic trioxide. However, based on the available evidence, conventional wastewater treatment methods such as neutralization and precipitation and solid waste disposal such as landfills are clearly inadequate for high-arsenic wastes. Careful treatment must be provided to prevent fugitive emissions, discharge into waterways, or leaching into water supplies. A review of wastewater treatments is contained in Patterson and Minear's publication for the State of Illinois (5).

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(5) Patterson, J. W. and Minear, R. A., Wastewater Treatment Technology, Second Edition, State of Illinois, Institute of Environmental Quality, January 1973.

SECTION 6

REGULATORY ACTION

The following list of regulatory actions, control options, attendant impacts, and personnel contacts has been prepared to show present Federal activities concerning arsenic (6):

- Air Pollution Assessment--An assessment of arsenic as an air contaminant includes a summary of the analysis of the National Air Sampling Network samples and other air samples around nine smelters. The final report deadline was mid-1976. Josephine Cooper, OAQPS, (919) 688-8146, X-501.

- Effluent Guidelines--The revision of best available technology limitations will include considerations of arsenic. A broad examination is being directed to the best approach for controlling arsenic. Guidelines for some industrial categories can be expected within the next two years. Ernst Hall, OWPS, (202) 426-2576.

- Hazardous Material Spills--Arsenic is included in the preliminary listing of hazardous chemicals under Section 311 of FWPCA. Mandatory reporting of any spill and clean-up and civil penalties are contemplated. Promulgation of the final regulation has been considered for late 1976. Allen Jennings, OWPS, (202) 245-0607.

- Interim Drinking Water Standards--A maximum permissible concentration of 0.05 g/m^3 for arsenic in drinking water has been promulgated. This concentration is currently being reviewed in connection with the development of additional standards in 1977. Joseph Cotruvo, OWS, (202) 766-5643.

- New Source Performance Standards--Arsenic data are being collected from process sources at primary copper, zinc, and lead smelters. Whether standards are set under Section

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(6) Identification of Selected Federal Activities Directed to Chemicals of Near-term Concern. EPA-560/4-76-006, U.S. Environmental Protection Agency, Washington, D.C., July 1976. 36 pp.

111 of the Clean Air Act is contingent on these data and the air pollution assessment. The overall study will take two years. Alfred Vervaert, OAQPS, (919) 549-8411, X-301.

- Review of Arsenical Pesticides--Arsenic is a candidate for rebuttable presumption proceeding under Section 3 of FIFRA. The determination deadline under this proceeding was May 1977. Ronald Dreer, OPP, (202) 755-5687.

- Water Quality Criteria--A concentration of 50 mg/m^3 has been proposed for total arsenic as a water quality criterion. David Critchfield, OWPS, (202) 245-3042.

- Workplace Standards--Revised arsenic workplace standards were proposed in January 1975. The final review of the inflationary impact statement is being completed. After this review and hearings, the final standard may be promulgated. Gerald Weinstein, OSHA, (202) 523-7186.

Arsenic is designated a priority pollutant under the Federal Water Pollution Control Act.

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APPENDIX

PRIMARY COPPER PRODUCTION

REVERBERATORY SMELTING

Function

Copper smelting is the process of removing from a roasted or dried ore concentrate much of its iron and some undesirable impurities, leaving a molten mixture that can be processed efficiently by a copper converter. This is most often accomplished by other methods.

The reverberatory furnace is a large horizontal chamber into which ore and various fluxing materials are charged. The furnace is then heated by direct firing. As the temperature of the charge increases, a complex series of chemical reactions takes place, and the charge separates into three fractions. One fraction is SO_2 gas, which along with other volatiles, is mixed with the combustion gases and is carried out of the furnace. A second fraction is a molten slag containing much of the iron, which is tapped from the furnace and discarded. The third fraction, called the matte, becomes the charge to the copper converter.

The charge to the reverberatory furnace is proportioned so that the resulting matte typically contains 40% to 45% copper and 25% to 30% each of iron and sulfur. The matte contains most of the heavy elements present in the charge, practically all the gold and silver, and part of the arsenic and antimony.

Reverberatory smelting, the oldest of the copper smelting processes now in use, is little different now than when it was first practiced in 1879. It is in use at all but two of the smelters in this country, in one of two modifications, described as either "deep bath" or "dry hearth". Some reverberatory furnaces are very large, capable of accepting as much as 1,800 metric tons of material per charge.

Input Materials

The primary input material is the roasted or dried concentrate, whose composition is not much different from the concentrate received from the mill. Slags from the converter and anode

furnace also are added for reprocessing, as are flue dusts from dust collection equipment throughout the smelter. Precipitates from hydro-metallurgical operations or materials from refinery processing may be added at this step.

Flux consists normally of sand high in silica content, and usually limestone to make the slag more fluid. Sometimes "direct smelting ore" is used, which adds both fluxing material and additional copper.

Composition of one charge to a reverberatory furnace in Arizona is reported as follows:

Ore concentrate	- 64%
Converter slag	- 2%
Precipitator	- 1%
Flue dusts	- 1%
Silica flux	- 2%
Limestone flux	- 6%

This charge produced molten materials of which 47% was matte and 53% was slag.

Operating Conditions

When possible, the concentrate is charged into the furnace while still hot from the roaster (400°C or more). Converter slag is charged as a liquid (approximately 1,100°C). Other materials are usually charged at ambient temperatures. The reverberatory furnace usually heats the mixed charge to at least 1,000°C before the matte forms and separates; temperatures up to 1,300°C have been reported. All operations are at or near atmospheric pressure.

Utilities

It is estimated that 90% of the energy consumed in a smelting operation is added into the reverberatory furnace. It is reported that 6.48×10^{16} J of energy were used in domestic copper smelters in 1973. Consumption of energy by this process is very high; it is usually supplied by natural gas, but pulverized coal or fuel oil can be used. It is estimated that 2.09×10^{9} J of heat is required to smelt 1 metric ton of concentrate if the charge is preheated by a roasting operation. If the charge is not preheated, an addional 1.63×10^{9} J are required. These values give credit for steam generated by waste heat boilers, which are almost always installed with a reverberatory furnace. In itself, the reverberatory furnace is thermally inefficient, using more than four times the heat theoretically required.

Noncontract cooling water is used by copper smelters, primarily for the protection of equipment auxiliary to the roaster, converter, and reverberatory furnace. Data that allocate this cooling load specifically to each process are not available. Reported data indicate that the total cooling water consumption for smelting operations can vary from 4 m^3 to 61 m^3 per metric ton of copper product.

Contact cooling water is used at four smelters to granulate the slag from the reverberatory furnace. One smelter uses 1,700 m^3 of water per day for this purpose.

Waste Streams

It is reported that 20% to 45% of the sulfur that enters with the ore concentrate is emitted by the reverberatory furnace as SO_2. Although most smelter operators have attempted to make operational changes either to increase or reduce this quantity, no recent data are available. The gas is released as a dilute stream of variable composition, reported as from 0.5 to 2.5 weight percent SO_2. Other constituents in the exit gas are shown in Table A-1, for unroasted and roasted concentrate feeds. The volume of this gas is very large, since it consists primarily of the combustion gases from the heating fuels. Temperature of the exit gases may reach 1,150°C to 1,200°C.

TABLE A-1. COMPOSITION OF REVERBERATORY FURNACE EXHAUST GASES

Component	Green feed, %	Calcined feed, %
Carbon dioxide	8.4	10.2
Nitrogen	69.3	71.0
Oxygen	0.25 to 1.0	0.25 to 1.0
Water	18.8	17.7
Sulfur dioxide	1.5 to 2.5	0.6

Between 14 kg and 40 kg of particulate matter are emitted in this gas stream per metric ton of copper matte produced. One analysis of the particulates showed 24% copper and the following concentrations of other elements:

Element	g/m^3
Zinc	44,000
Cadmium	310
Manganese	100
Chromium	45
Nickel	35
Mercury	2.5

Other investigations indicate that most of the volatilized arsenic, selenium, lead, antimony, cadmium, chromium, and zinc emissions will be generated in the reverberatory furnace.

Fugitive dust is generated in this process as materials are loaded into the furnace. No quantities are reported, but this is probably one of the largest sources of dust in a smelting operation.

The only liquid waste from this process is the run-off from slag granulation. Three complete analyses are reported as shown in Table A-2. Liquid waste is most often generated as the overflow from a pond into which the molten slag is dumped. Since the pond is an open body of usually hot water, subject to rainfall and evaporation, quantity and composition of the overflow may be highly variable.

TABLE A-2. EFFLUENTS FROM SLAG GRANULATION (g/m^3)

Parameter	Plant 103	Plant 110	Plant 102
pH	7.7	8.1	6.4 to 7.6
Total dissolved solids	140	3,800	-[a]
Total suspend solids	6.8	151	-
Sulfate	62	310	-
Cyanide	0.005	0.050	0.030
Arsenic	3.7	0.048	5.70
Cadmium	0.001	0.001	0.042
Copper	0.12	0.05	0.604
Iron	0.04	0.03	340
Lead	0.04	0.070	7.4
Mercury	0.0001	0.0001	0.0001
Nickel	0.001	0.06	0.16
Selenium	0.001	0.54	0.040
Tellurium	0.001	-	0.100
Zinc	0.44	0.023	36
Oil and grease	-	0.0	0.02

[a]No data available.

One copper smelter is situated close to a market for the furnace slag it produces; for all the others, the slag constituted a large quantity of solid waste, as much as 3,000 kg/metric ton of copper produced. Table A-3 gives an analysis of potentially hazardous elements found in a reverberatory furnace slag. The bulk of the slag is a mixture of iron silicates, with other elements, also as shown in Table A-3.

TABLE A-3. GENERAL RANGE OF REVERBERATORY FURNACE SLAG COMPOSITION

Compound or element	Composition, %
Iron oxide	34 to 40
Silicon dioxide	35 to 40
Calcium oxide	3 to 7
Magnesium oxide	0.5 to 3
Aluminum oxide	4.5 to 10
Copper	0.4 to 0.7
Sulfur	0.0 to 1.5

Trace elements	ppm
Zinc	7,800
Maganese	450
Antimony	400
Lead	100
Chromium	100
Selenium	20
Nickel	25
Cadmium	10
Mercury	1.0
Arsenic	Trace
Tellurium	Trace
Cobalt	Trace

Control Technology

Gases from the reverberatory furnace pass through a waste heat boiler and then through an electrostatic precipitator for particulate removal. The gases may pass through spray coolers or balloon flues before entering the ESP units. The degree of particulate removal ranges from 50% to 99.9%. Particulates collected are recycled into the metallurgical process, normally as part of the reverberatory furnace charge, but accumulations of trace elements causes some flue dusts to be discharged or processed separately. Quantities and their disposition are not reported.

At present, there is virtually no control of the SO_2 emissions from reverberatory smelters. Intensive studies are underway to develop scrubbing techniques that can be applied to large volumes of flue gas containing small concentrations of SO_2. These represent the best available control technology. One smelter absorbs the SO_2 from this stream in dimethyl aniline and regenerates it as a concentrated stream for further processing.

One Canadian smelter uses an ammonia absorption process on some streams, but this system is not in use in this country. Other scrubbing solutions, containing compounds of zinc and aluminum, are used on smelter gases in Japan. Scrubbers using lime or limestone, with and without magnesium addition, are being used on sulfur-containing flue gases from coal-fired boilers in the United States, and might be adopted for use in U.S. smelters, as has been done in Japan. Another absorption process based on sodium sulfite-bisulfite is under test. The only one of these processes specific to the domestic copper industry is DMA absorption.

Of the four smelters that practice slag granulation, one reports no wastewater from this source, since the rate of evaporation at this location necessitates a continuous water make-up to the quenching pond. The other three smelters mix the water from slag granulation with other wastes.

Granulated slag is usually a coarse-grained material of low to medium density, usually discarded near the smelter. A small amount may find a market for use as road fill or concrete aggregate. Crushed slag that has not been granulated also finds a small market for these same purposes. Most slag is not granulated, but is simply poured out and allowed to solidify. There is no easy way to naturalize or reclaim the slag dumping areas, and there are no published reports on how this could be done. It is generally assumed that the potential of secondary water pollution from slag dumps is less than that from mine spoil or tailings beds.